RPM-2: A recyclable porous material with unusual adsorption capability: self assembly via structural transformations

Long Pan,[a] Haiming Liu†,[b] Sean P. Kelly,[a] Xiaoying Huang,[a] David H. Olson[b] and Jing Li*[a]

[a] Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA.
E-mail: jingli@rutchem.rutgers.edu

[b] Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

Structural transformation via deliberate and partial topological changes in a grid network structure has led to a three-dimensional, fully recyclable porous material (RPM-2) with a very high sorption capability.

Self-assembly of molecular electronics and smart materials will bring a new era in the field of material science.[1] However, effective control of a self-organization process towards targeted products still remains an enormous challenge in both static self-assembly and dynamic self-assembly.[2] Realization of new crystalline architectures with desired topology and specific properties often suffers from numerous factors that are difficult to control, for example, various ways in which a metal and a ligand may form a bond and different geometries that a metal may adopt, as well as unforeseen ways of crystal packing. While much effort has been made recently in this regard,[3] accurate prediction of structures for even the simplest type of crystalline solids from a knowledge of their chemical composition is still unachieved.[4] We and others have noted that partial topological changes of a framework can be achieved effectively through structural transformations.[5] The secondary building unit (SBU)[6] approach may be extended to include 1D and 2D structural motifs. Assembly of a targeted 3D structure using these structural motifs can, thus, be carried out in a more controllable manner, due to their well-defined topology and rigid backbone structure that effectively reduce the unpredictable factors. Scheme 1 illustrates such an example where a 2D structure (or SBU) transforms to a 3D network by a simple ligand exchange. Furthermore, if such a transformation is reversible between a porous and a nonporous structure, some important applications can be envisioned. Our recent exploratory study on such a structure, the 3D porous RPM-1 (RPM: Rutgers Recyclable Porous Material) system,[7] has demonstrated its potential to be used as a host material in "ship-in-bottle" synthesis. Herein, we report another 3D porous compound, RPM-2, obtained by a structural transformation from a 2D precursor (or SBU). In the present case, the 2D sheets of the 2D structure are present in the 3D structure but as interpenetrating pairs of identical sheets, requiring a partial restructuring of the single 2D sheets during the transformation. The process is fully recyclable.

Using 2D [Co(bpdc)(py)$_2$]·H$_2$O (1)[5a] as a precursor, 3D structure [Co(bpdc)(bpy)]·0.5DMF (2) (bpy = 4,4'-bipyridine,

bpdc = biphenyldicarboxylate, DMF = dimethylformamide), or RPM-2, was assembled by mixing 1 and bpy in the molar ratio of 1:4 in 5 mL of DMF at 120 °C for one day under autogenous pressure in a Teflon-lined autoclave. Orange needle-like crystals of 2 were obtained in 90% yield.[8] Compound 2 was insoluble in common solvents such as methanol, DMF, ether, acetonitrile, CHCl$_3$, benzene and toluene. However, it can be readily transformed to a 1D [Co(bpdc)(H$_2$O)$_2$]·H$_2$O (3)[5a] structure upon immersion in a hot water/ethanol solution.[8] Upon a mild chemical process, structure 3 can be converted back to 1,[5a] thus completing the cycle (see below).

$$1 \text{ (2D)} \rightarrow 2 \text{ (3D)} \rightarrow 3 \text{ (1D)}$$
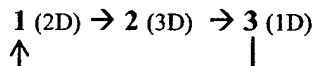
X-ray analysis‡ performed on a single crystal of 2 revealed a porous structure (Fig. 1) possessing a three-dimensional network containing rectangular-shaped 1D open channels along the a-axis (window size: ~5.6 × 3.0 Å). Fig. 2 shows the structural relation between 1 and 2. Structure 1 is a 2D network built on Co$_2$(bpdc)$_4$(py)$_4$ basic building blocks (Fig. 2a). Its backbone structure, Co(bpdc), is a 2D motif shown in Figure 2b. Each Co of the Co$_2$ pair in the building block is four-fold coordinated to oxygen atoms through chelating and μ_2-bridging carboxylate ions of bpdc, forming a noninterpenetrating 2D lattice with quadrilateral shaped grids (Fig. 2b). Structure 1 is resulted by completing the metal octahedral coordination with four pyridines going into the apical positions (two per metal). The same Co(bpdc) motif forms the backbone structure of 2, except that the 2D lattice now contains two identical, inter-penetrating units (Fig. 2d). Replacing apical pyridines by exo-bidentate ligand 4,4'-bpy results in 3D porous network structure 2.

The basic building block of 2, Co$_2$(bpdc)$_4$(bpy)$_4$, is shown in Figure 2c. Unlike in 1, where the two benzene rings of bpdc are essentially in plane, they are severely bent in 2 (the dihedral angles of the two benzene rings in two bpdc are 41.20 and 17.25°, respectively). This distortion[9] is required to make room to accommodate the two interlocking Co(bpdc) layers (Fig. 3). As a result, the planar lattice of quadrilateral shaped grids in 1 is replaced by an undulating network with irregular rhombus (Fig. 3). Interconnection of the adjacent wave-like layers by
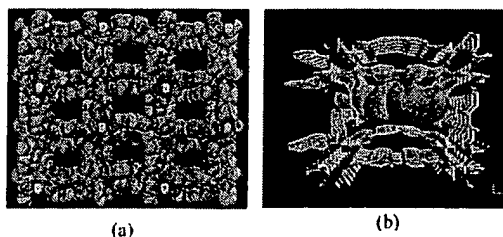

Scheme 1

(a)   (b)
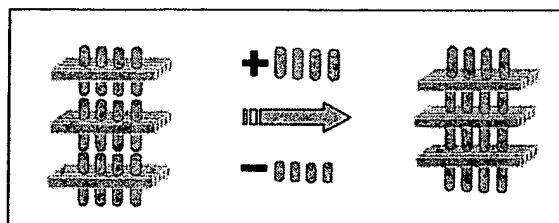
Fig. 1 (a) View of RPM-2 (2) structure along the a-axis. (b) View showing a 1D open channel filled with DMF solvent molecules.
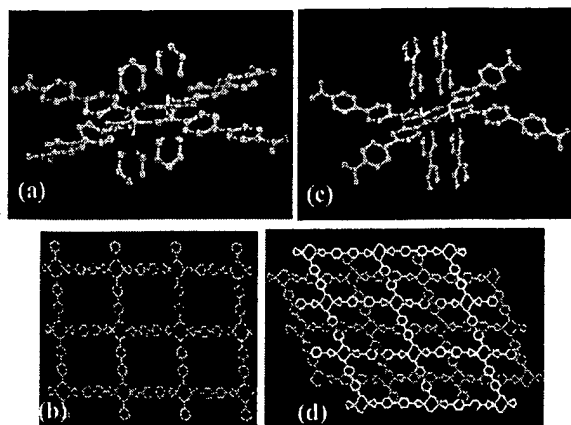
Fig. 2 (a) Basic building block [Co$_2$(bpdc)$_4$(py)$_4$] in **1**. Co (light blue), O (red), N (blue), C (gray). (b) 2D Co(bpdc) backbone structure motif in **1**. (c) Basic building block [Co$_2$(bpdc)$_4$(bpy)$_4$] in **2**. (d) Two-dimensional slab in **2** composed of two identical and interpenetrating Co(bpdc) backbone structure motifs.

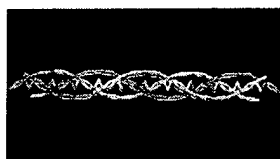**Fig. 3** Side view of the two identical and interlocking Co(bpdc) layers in **2**.

4,4'-bpy as pillars gives rise to a non-interpenetrating 3D framework with 1D rectangular channel (~ 5.6 × 3 Å based on van der Waals radius of carbon) running along the *a*-axis. (Fig. 1a). The solvent molecules (DMF) are arranged in a head-to-tail fashion within every channel (Fig. 1b). Calculation of the pore volume in **2** reveals that 28.6% of the structure is occupied by guest molecules.

Under nitrogen environment, thermogravimetric analysis (TGA) performed on the as-synthesized RPM-2 showed one-step weight loss of DMF in the range of 160–200 °C. The framework structure is stable up to 350 °C. PXRD analysis indicated Co$_3$O$_4$ as the only residue after the sample was heated to 700 °C. For gas adsorption experiments, the sample was heated to 200 °C to remove the guest molecules. The PXRD pattern showed no change compared to the simulated pattern produced from the single crystal XRD based structure.

RPM-2 displays high (reversible) sorption capacity for hydrocarbons (Table 1), despite its small 1D channels. While its adsorption properties resemble those of zeolites they are clearly

Table 1 Sorption properties of RPM-2

Hydrocarbon	$P/P^{o a}$	Sorption (wt.%)
Propene	0.063	11
n-Hexane	0.48	10
Cyclohexane	0.45	9
p-Xylene	0.34	11
o-Xylene	0.37	15
Mesitylene	0.27	11
Triisopropylbenzene	~0.9	1

^{a} P is the sorption partial pressure of a sorbate, and P^o is the calculated vapor pressure at the sorption temperature at 30 °C.

unique owing to its hydrocarbon based surface and distinctive pore structure. The adsorption capacities range from 9 to 15 wt% for the sorbed gases. The uptake of large molecules such as cyclohexane, xylenes and mesitylene is unexpected for RPM-2 with a channel opening of 5.6 × 3 Å. In particular, the uptake of large mesitylene molecules, which are too large for ZSM-5, a zeolite with 5.5 × 5.5 Å channels, is surprising. This suggests flexibility of RPM-2's channel windows (composed of aromatic hydrocarbons) and also reflects the difficulty of precisely calculating the pore size of the hydrocarbon based pores. Triisopropylbenzene (8.5 Å) is excluded, consistent with RPM-2's pore diameter. At 30 °C, RPM-2's adsorption capacity for ortho-xylene, 15 wt% (0.17cm^3 g^{-1}), is unusually larger than for other hydrocarbon gases (~ 10 wt%). Also, an unexpected increase in o-xylene capacity is observed for 60 → 40 °C, ~ 4 wt% while for p-xylene the difference is only ~ 1 wt%. This is attributed to more efficient packing of o-xylene. The isosteric heat of adsorption of n-hexane at zero coverage of ~ 68 kJ $^{-1}$ was obtained from adsorption isotherms. This heat of sorption is considerably larger than that of H–Y (45.5 kJ mol^{-1}), and is close to that of H-ZSM-5 (68.8 kJ mol^{-1}).[10] The heat of sorption for RPM-2 is close to that for RPM-1 (66 kJ mol^{-1})[7] indicating that both RPM-1 and RPM-2 interact strongly with n-hexane.

In conclusion, deliberate replacement of ligands via a structural transformation of a coordination motif has led to a porous 3D network with essentially the same backbone structure. This network structure can be recycled via a three-step process. This approach may become a practical route for partial modification of structure topology in crystal engineering. The porosity and unusual sorption capability of RPM-2 are of significant interest for applications in sorption, separation, and shape-selective reactions.

Notes and references

1 (a) R. F. Service, *Science*, 2002, **295**, 2398; (b) M. D. Hollingsworth, *Science*, 2002, **295**, 2417.
2 G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418.
3 (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
4 J. Maddox, *Nature*, 1988, **335**, 201.
5 (a) L. Pan, N. Ching, X.-Y. Huang and J. Li, *Inorg. Chem.*, 2000, **39**, 5333; (b) L. Pan, N.-W. Zheng, Y.-G. Wu, S. Han, R.-Y. Yang, X.-Y. Huang and J. Li, *Inorg. Chem.*, 2001, **40**, 828; (c) G. Yang and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 8389; (d) J. D. Ranford, J. J. Vittal, D.-Q. Wu and X.-D. Yang, *Angew. Chem., Int. Ed.*, 1999, **38**, 3498.
6 J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239.
7 L. Pan, H.-M. Liu, X.-G. Lei, X.-Y. Huang, D. H. Olson, N. J. Turro and J. Li, *Angew. Chem., Intl. Ed.*, 2003, **42**, 542.
8 Upon immersing in hot water/ethanol solution (volume ratio 1:10), RPM-2 (**1**) was transferred to, 3 completely.
9 (a) M. W. Haenel, H. Irngartinger and C. Krieger, *Chem Ber.*, 1985, **118**, 144; (b) G. C. Bazan, W. J. Oldham, Jr., R. J. Lachicotte, S. Tretiak, V. Chernyak and S. Mukamel, *J. Am. Chem Soc.*, 1998, **120**, 9188.
10 J. F. Denayer, W. Souverijns, P. A. Jacobs, J. A. Martens and G. V. Varon, *J. Phys. Chem. B*, 1998, **102**, 4588.